

Crystal Structures of the Clathrate Inclusion Compounds Formed by the Host Bis(Isothiocyanato) tetrakis (4-methylpyridine) iron (II) with Benzene, *m*-Xylene and *p*-Xylene as Guests

JANUSZ LIPKOWSKI

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01 224 Warsaw, Poland

(Received: 20 February 1989; in final form: 18 April 1989)

Abstract. Single crystal X-ray structures of three 1:1 (guest:host) compounds in which the $\text{Fe}(\text{NCS})_2(4\text{-methylpyridine})_4$ complex is the host component and benzene, *m*-xylene and *p*-xylene are the respective guest components, are reported. The crystals of the inclusion compounds are tetragonal $I4_1/a$, with: $a = 17.08(1)$, $c = 23.66(3)$ Å (benzene clathrate); $a = 17.17(1)$, $c = 24.02(2)$ Å (*m*-xylene clathrate) and $a = 17.12(1)$, $c = 23.93(3)$ Å (*p*-xylene clathrate); $Z = 8$. The host complex molecule has the octahedral type of coordination of the N_6 donor system. The isothiocyanate ligands are in *trans* positions and related by twofold axial symmetry. The symmetry axis runs diagonally between the neighbouring, equatorial 4-methylpyridine (MePy) ligands. The two symmetrically independent MePy ligands form angles of *ca.* 45 and 55° with the equatorial Fe– N_4 plane. The absorption sites for guest molecules lie on centres of symmetry. Non-centrosymmetric *m*-xylene molecules occupy these sites randomly distributed over two orientations related by symmetry. The structures belong to the class of *organic zeolites* since the cavities occupied by the guest molecules are interconnected to form a three-dimensional network.

Key words. Clathrate, organic zeolite, crystal structure.

1. Introduction

The title host complex, $\text{Fe}(\text{NCS})_2(4\text{-MePy})_4$ (MePy = methylpyridine) shows, similar to the analogous complexes of the general formula MX_2A_4 [1], the ability to form inclusion type crystalline compounds with organic molecules entrapped as the guest component. In contrast to the analogous compounds containing nickel or cobalt complexes as hosts the title compounds shows a dramatic difference in colour. This varies from light yellow (*m*-xylene clathrate, [II]) through light brown (benzene compound [I]) to deep black (*p*-xylene clathrate [III]). This observation may suggest interesting electronic intermolecular interactions in compounds I and III which, in turn, was the reason for undertaking this study.

2. Experimental

The crystals were precipitated by cooling to room temperature hot solutions containing $\text{Fe}(\text{SCN})_2$, 4-MePy and the respective guest. 4-MePy and guest compounds were used in excess quantities with respect to the clathrate stoichiometry. The amount of 4-MePy added to $\text{Fe}(\text{SCN})_2$ was twice the stoichiometric amount, the guest was used in a very large excess as one component of the solvent mixture,

Table I. Data collection and structure analysis parameters

		I	II	III
Molecular formula	FeS ₂ N ₆ C ₂₆ H ₂₈ +	C ₆ H ₆	<i>m</i> -(CH ₃) ₂ C ₆ H ₄	<i>p</i> -(CH ₃) ₂ C ₆ H ₄
Molecular weight		624.8	650.8	650.8
Unit cell	<i>a</i>	17.08(1)	17.17(3)	17.12(1)
(in Angstrom units)	<i>c</i>	23.66(3)	24.02(5)	23.93(3)
	<i>V</i>	6902(10)	7081(23)	7013(11)
	<i>Z</i>	8	8	8
Density (calc.) [g cm ⁻³]		1.202	1.221	1.233
Space group		<i>I</i> 4 ₁ / <i>a</i>	<i>I</i> 4 ₁ / <i>a</i>	<i>I</i> 4 ₁ / <i>a</i>
Radiation			graphite monochromatized Mo K _α	
Absorption coefficient [cm ⁻¹]		5.38	5.24	5.29
Crystal size [mm]		0.3 × 0.4 × 0.4	0.4 × 0.4 × 0.5	0.3 × 0.3 × 0.2
Number of reflections				
measured		7992 ^a	4602	5571 ^a
unique		2517	2125	1694
used in the structure analysis		2113	2116	1261
Final <i>R</i> values				
unweighted		0.072	0.051	0.065
weighted		0.071	0.057	0.059
$w = k/(\sigma^2(F) + m \times F \times F)$	<i>k</i>	1.000	0.400	1.000
	<i>m</i>	0.002	0.0007	0.0003
Residual extrema in				
final difference map		0.76	0.29	0.41
Refined site occupation				
factor for guest		0.820(16)	1.01(1)	1.02(1)

^a The data were measured in triclinic I centered cells with the *a* and *c* parameters close to those given in the table. Structures I and III were then solved in the triclinic cells. Next, it was found that a lattice transformation by using the matrix [0.5 0.5 0.5 / -0.5 -0.5 0.5 / 1 -1 0] leads to the final, tetragonal cells, as given above. For this reason the number of data measured is high compared with the number of unique data. The Author wishes to express the opinion that the so-called 'pseudotetragonal' or 'pseudo beta' structures reported recently in the literature of Werner clathrates, which are claimed to be triclinic with I centered lattices and having pseudotetragonal unit cells, can be transformed into actual tetragonal ones by a transformation of the type given above.

the other was ethanol as the solvent for Fe(SCN)₂. The clathrate crystals obtained are unstable in open air. Thus, X-ray studies were performed by using crystals placed in glass capillaries together with droplets of the respective mother solutions. A summary of experimental data on the X-ray diffraction is given in Table I.

The structures were solved by the Patterson method followed by partial structure expansion (SHELXS [2]) and refinement (SHELX 76 [3]). No attempts to locate hydrogen atoms were made – hydrogens were included in the final refinement cycles at geometrically calculated positions (C–H distance 1.08 Å) as 'riding' on respective carbons or as elements of rigid CH₃ groups. The numeric details of the results of the refinement are included in Table I.

3. Results and Discussion

The atomic coordinates are listed in Table II. In Figure 1 the atom numbering scheme and an ORTEP drawing of the host molecule are given. The molecule

adopts a four-bladed 'propeller' conformation of the four pyridine rings. The geometry of the $\text{Fe}(\text{NCS})_2(4\text{-MePy})_4$ molecule in all three compounds is almost exactly the same, as may be seen from a comparison of bond distances and angles and conformational angles, given in Table III, and from the listing of selected conformational angles given in Table IV. The structure of the host molecule is close to that of the $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4$ molecule in tetragonal clathrates [7] (with obvious differences in the coordination bond lengths).

The molecular packing in the structures is illustrated in the projection given in Figure 2. This is, in principle, consistent with van der Waals packing of the host and guest molecules. However, in the xylene clathrates a few of the intermolecular

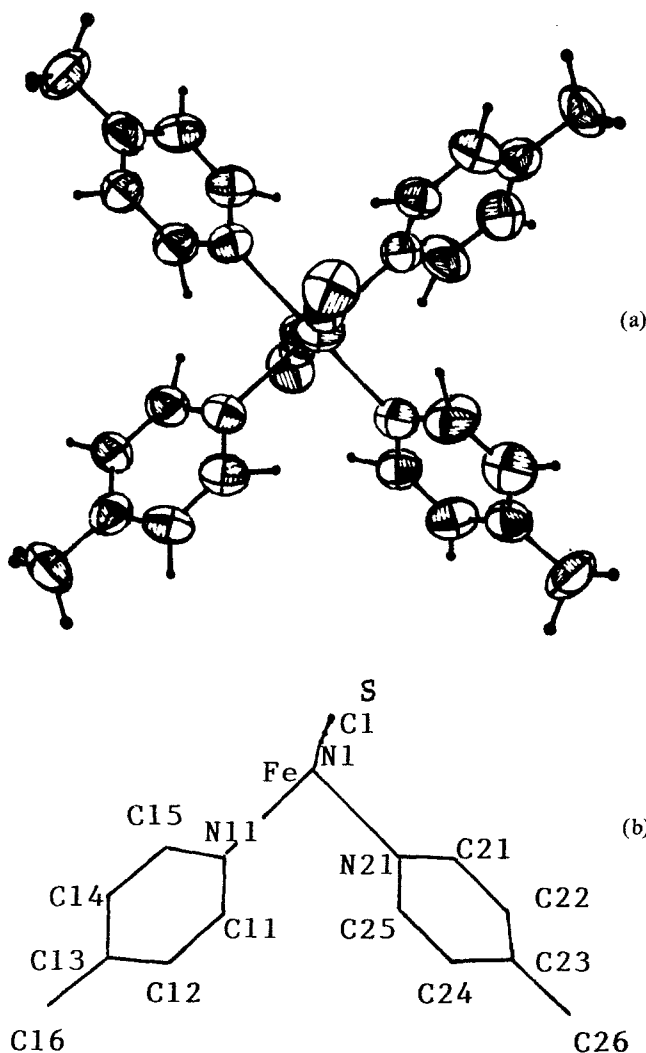


Fig. 1. (a) ORTEP [4] plot of the host molecule (*p*-xylene clathrate) and (b) the atom numbering scheme given for the asymmetric part of the molecule.

Table II. Atomic coordinates (fractional $\times 10^4$), estimated standard deviations (in parentheses) and mean temperature factors for non-hydrogen atoms

Atom	x/a	y/b	z/c	B_{equiv}
<i>I. Benzene clathrate</i>				
host				
Fe	0	2500	544(0.5)	3.74(3)
S	7476(1)	1208(1)	533(1)	6.83(5)
C(1)	8361(3)	1552(3)	529(2)	3.97(11)
N(1)	8992(3)	1784(2)	524(2)	5.07(12)
N(11)	496(2)	1732(2)	1219(2)	4.59(11)
C(11)	1244(3)	1574(3)	1274(2)	4.75(14)
C(12)	1549(3)	1125(3)	1704(2)	5.63(15)
C(13)	1063(4)	822(3)	2115(2)	5.73(16)
C(14)	285(4)	988(4)	2055(3)	6.86(20)
C(15)	21(4)	1431(4)	1607(2)	6.28(18)
C(16)	1367(5)	341(4)	2603(3)	8.40(23)
N(21)	572(2)	1769(2)	129(2)	4.00(10)
C(21)	556(3)	989(3)	132(2)	4.43(13)
C(22)	908(3)	540(3)	549(2)	4.76(13)
C(23)	1288(3)	892(3)	992(3)	4.55(13)
C(24)	1314(3)	1707(3)	985(2)	4.72(13)
C(25)	957(3)	2114(3)	554(2)	4.55(13)
C(26)	1664(4)	433(4)	1472(3)	6.99(20)
guest				
C(B1)	7774(13)	1970(8)	2141(8)	11.61(59)
C(B2)	7097(12)	2318(9)	2007(7)	12.16(57)
C(B3)	6824(9)	2886(8)	2402(9)	11.25(53)
<i>II. m-Xylene clathrate</i>				
host				
Fe	5000	2500	1983(0.7)	4.89(2)
S	6295(1)	-1(1)	2030(1)	7.64(5)
C(1)	5951(2)	877(3)	2011(2)	4.80(10)
N(1)	5717(2)	1501(2)	2006(2)	5.90(12)
N(11)	5763(2)	3003(2)	1321(2)	5.33(10)
C(11)	5897(3)	3765(3)	1255(2)	5.72(13)
C(12)	6347(3)	4055(3)	830(2)	6.32(14)
C(13)	6668(3)	3580(3)	445(2)	6.08(14)
C(14)	6533(3)	2792(3)	504(2)	7.61(18)
C(15)	6089(3)	2533(3)	948(2)	7.17(17)
C(16)	7142(3)	3872(4)	-46(3)	8.34(18)
N(21)	5726(2)	3065(2)	2644(2)	5.13(10)
C(21)	6509(3)	3059(2)	2645(2)	5.58(13)
C(22)	6958(3)	3406(3)	3049(2)	5.84(14)
C(23)	6614(3)	3787(3)	3486(2)	5.46(13)
C(24)	5807(3)	3803(3)	3484(2)	5.57(13)
C(25)	5397(3)	3451(3)	3070(2)	5.62(13)
C(26)	7079(4)	4167(4)	3942(2)	8.00(18)
guest				
C(X1)	6989(10)	2638(11)	2019(9)	16.50(1.72)
C(X2)	7656(10)	3099(11)	1975(9)	16.88(1.18)
C(X3)	8227(10)	3064(11)	2387(9)	10.25(0.73)
C(X4)	8133(10)	2569(11)	2843(9)	7.59(0.57)
C(X5)	7466(10)	2108(11)	2886(9)	9.72(0.67)

Table II. (Continued)

Atom	x/a	y/b	z/c	B_{equiv}
C(X6)	6894(10)	2143(11)	2474(9)	13.10(1.18)
C(X7)	6015(25)	2184(20)	2058(24)	26.81(3.09)
C(X8)	8656(19)	2511(24)	3375(13)	16.48(1.46)
III. <i>p</i> -Xylene clathrate				
host				
Fe	5000	7500	1977(1)	4.51(5)
S	3702(1)	4988(1)	2013(1)	6.41(8)
N(1)	4289(4)	6493(4)	1996(3)	5.24(21)
C(1)	4048(5)	5858(5)	2006(3)	4.28(26)
N(11)	4239(4)	8000(4)	1317(3)	4.70(21)
C(11)	4086(5)	8754(5)	1245(4)	4.84(29)
C(12)	3647(5)	9045(5)	813(4)	5.80(30)
C(13)	3322(5)	8550(6)	425(4)	5.49(30)
C(14)	3483(6)	7768(6)	491(4)	6.57(36)
C(15)	3932(6)	7524(5)	932(5)	6.84(35)
C(16)	2849(5)	8858(6)	68(4)	7.46(32)
N(21)	4281(4)	8073(4)	2645(3)	4.65(22)
C(21)	4604(5)	8452(5)	3073(4)	5.11(29)
C(22)	4200(5)	8805(5)	3491(4)	4.88(29)
C(23)	3393(6)	8791(5)	3490(4)	5.06(30)
C(24)	3039(5)	8412(5)	3054(4)	5.30(29)
C(25)	3476(5)	8064(5)	2646(4)	5.04(29)
C(26)	2916(6)	9165(6)	3953(4)	7.42(36)
guest				
C(X11)	5434(6)	10034(8)	475(4)	7.25(34)
C(X12)	5528(6)	9422(7)	118(5)	7.40(38)
C(X13)	5095(7)	9370(7)	369(5)	7.20(39)
C(X14)	5202(9)	8686(9)	770(7)	13.68(67)

distances between atoms of the guest and host molecules are slightly, though significantly, less than the respective sums of van der Waals radii. This is illustrated in the section drawings given in Figures 3a and b and 4a, b and c. In particular, as may be seen in Figure 4b, the hydrogen atoms of the *p*-xylene guest molecule in *ortho* positions with respect to the methyl substituents are in close contact with sulphur atoms of the two neighbouring host complex molecules. The interatomic distance H(X11)—S of 2.92 Å is shorter than the respective sum of van der Waals radii (3.05 Å). It seems this is the most significant difference between the packing patterns of the *p*-xylene and the other two clathrates. In the *m*-xylene compound there are also short contacts between xylene hydrogens and the two adjacent isothiocyanate sulphur atoms but not simultaneously because of disordering, i.e. the short contacts are either with one sulphur or the other.

The conclusions of the present structural study are that:

- (i) the compounds studied belong to the class of *organic zeolites* [6] and are isostructural with the analogous nickel (II) and cobalt (II) clathrates;

Table III. Bond distances and angles with estimated standard deviations (in parentheses)

	I	II	III
Fe—N(1)	2.112(4)	2.112(4)	2.111(7)
Fe—N(11)	2.233(4)	2.234(5)	2.219(7)
Fe—N(21)	2.247(4)	2.239(5)	2.243(7)
S—C(1)	1.621(5)	1.619(5)	1.603(9)
C(1)—N(1)	1.148(7)	1.144(6)	1.163(11)
N(11)—C(11)	1.312(6)	1.317(6)	1.328(11)
N(11)—C(15)	1.328(7)	1.329(6)	1.338(13)
C(11)—C(12)	1.376(7)	1.373(7)	1.372(13)
C(12)—C(13)	1.379(7)	1.350(7)	1.375(13)
C(13)—C(14)	1.366(9)	1.380(7)	1.376(15)
C(13)—C(16)	1.509(8)	1.518(8)	1.525(15)
C(14)—C(15)	1.378(9)	1.384(7)	1.371(15)
N(21)—C(21)	1.332(6)	1.344(6)	1.333(12)
N(21)—C(25)	1.338(6)	1.343(6)	1.378(11)
C(21)—C(22)	1.386(7)	1.375(7)	1.358(13)
C(22)—C(23)	1.371(7)	1.370(7)	1.382(13)
C(23)—C(24)	1.392(7)	1.385(7)	1.370(13)
C(23)—C(26)	1.522(8)	1.504(7)	1.518(14)
C(24)—C(25)	1.376(7)	1.360(7)	1.367(13)
N(11)—Fe—N(21)	90.9(1)	90.6(2)	90.9(3)
N(1)—Fe—N(21)	91.0(1)	90.5(2)	91.5(3)
N(1)—Fe—N(11)	89.2(1)	89.5(2)	89.5(3)
S—C(1)—N(1)	178.9(4)	178.7(5)	178.9(8)
Fe—N(1)—C(1)	164.7(3)	164.9(4)	165.6(7)
Fe—N(11)—C(15)	119.3(3)	119.5(5)	119.1(6)
Fe—N(11)—C(11)	124.1(3)	124.3(4)	125.7(6)
C(11)—N(11)—C(15)	116.5(4)	116.2(6)	115.2(8)
N(11)—C(11)—C(12)	123.8(5)	122.6(7)	124.0(8)
C(11)—C(12)—C(13)	120.2(5)	121.3(7)	120.5(9)
C(12)—C(13)—C(16)	122.4(6)	123.5(8)	121.6(9)
C(12)—C(13)—C(14)	115.7(5)	117.0(6)	116.2(9)
C(14)—C(13)—C(16)	121.8(6)	119.6(7)	122.1(9)
C(13)—C(14)—C(15)	120.8(6)	119.1(7)	119.8(9)
N(11)—C(15)—C(14)	123.0(6)	123.8(8)	124.4(8)
Fe—N(21)—C(25)	120.1(3)	121.3(4)	123.0(6)
Fe—N(21)—C(21)	123.4(3)	123.7(5)	122.2(6)
C(21)—N(21)—C(25)	116.5(4)	115.0(5)	114.8(8)
N(21)—C(21)—C(22)	123.2(5)	124.0(6)	124.8(8)
C(21)—C(22)—C(23)	120.4(5)	120.4(5)	120.0(9)
C(22)—C(23)—C(26)	123.0(5)	122.4(6)	122.0(9)
C(22)—C(23)—C(24)	116.4(5)	116.0(6)	116.9(9)
C(24)—C(23)—C(26)	120.7(5)	121.6(6)	121.2(9)
C(23)—C(24)—C(25)	120.0(5)	120.8(6)	120.6(8)
N(21)—C(25)—C(24)	123.5(5)	124.0(5)	122.9(8)

Table IV. Selected torsion angles and interplanar angles (with standard deviations in parentheses)

	I	II	III
N(21)—Fe—N(1)—C(1)	141.8(1.8)	138.1(2.3)	-134.6(2.8)
Interplanar angles:			
I—II	126.8(2)	55.8(2)	125.7(3)
I—III	134.4(2)	45.5(3)	134.8(2)
I—IV	37.0(1.1)	69.8(5)	32.0(7)
II—III	68.2(2)	69.2(3)	68.6(3)
II—IV	112.1(1.2)	92.0(4)	154.8(8)
III—IV	98.1(1.1)	26.7(4)	132.9(8)

The plane defining atoms:

plane I: Fe, N11, N21

plane II: N11 through C15

plane III: N21 through C25

plane IV: non-hydrogen atoms of the guest molecule.

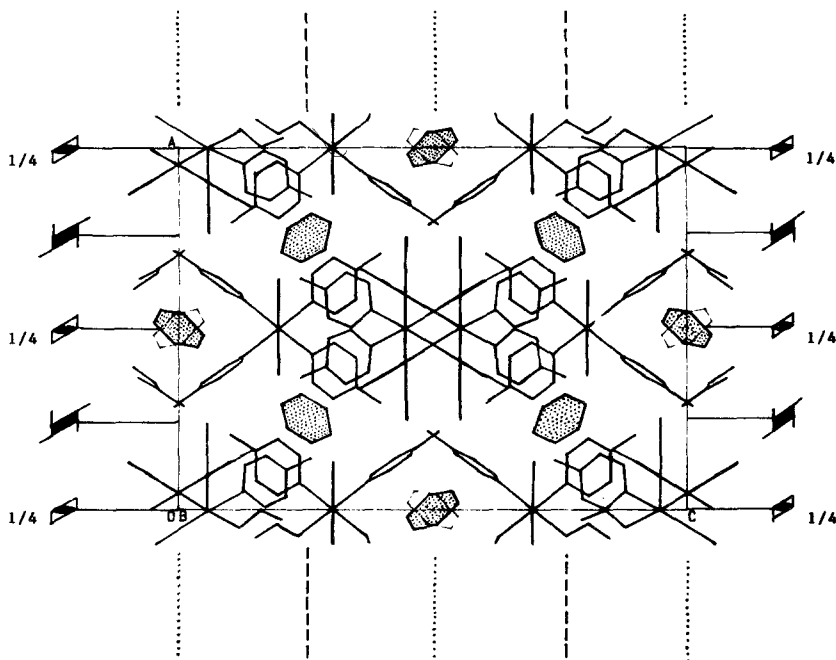


Fig. 2. The pattern of the molecular packing in the benzene clathrate of $\text{Fe}(\text{NCS})_2(4\text{-MePy})_4$ viewed as the projection of the unit cell content along the b crystal axis. For the sake of clarity: hydrogen atoms are omitted, the guest molecules are dotted and symmetry elements of the structure are shown in the diagram.

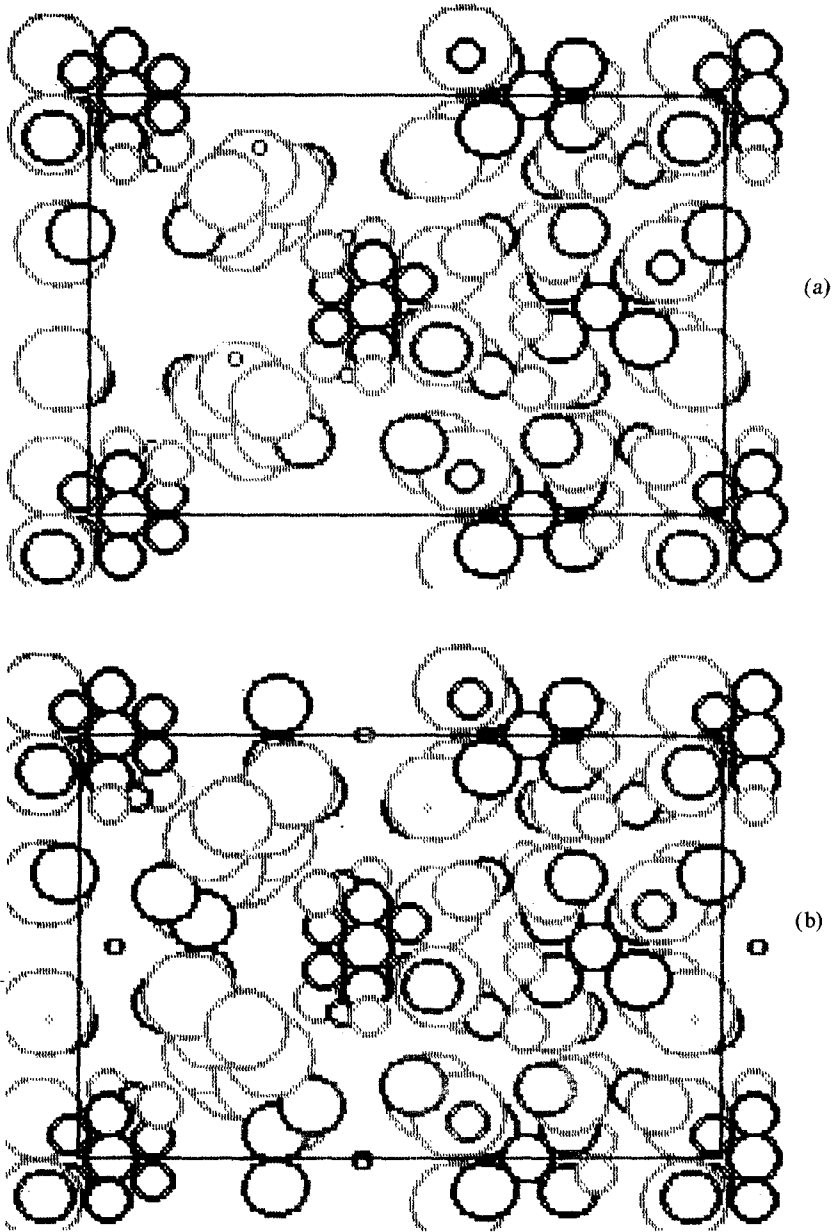


Fig. 3. Plane sections [5] through the structure of the benzene (a) and *p*-xylene (b) clathrates at $y = 0.25$. The orientation of the unit cell as in Figure 2.

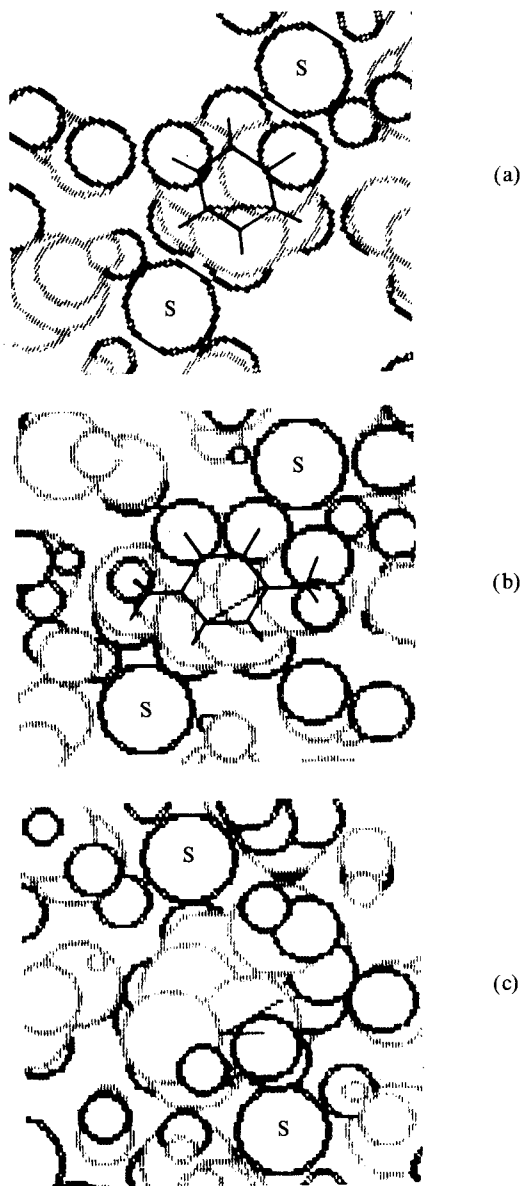


Fig. 4. Plane sections through structures I (a), II (b) and III (c) with the section planes defined by the guest ring atoms.

- (ii) no significant difference in the molecular geometry of the host in the compounds I, II and III, which could be associated with the different colours of the clathrates, is observed;
- (iii) there are some short guest–host intermolecular contacts of the type H—S which are, perhaps, the only significant *differentia specifica* between the three structures. Since the X-ray structural data give no information sufficient to

interpret the colour differences in the compounds studied, a separate study on the electronic structure of the clathrates was undertaken. The results will be reported separately, in due course.

Acknowledgement

The study was performed within the WPR-III/6 programme of PAN.

References

1. J. Lipkowski: 'Inclusion Compounds Formed by Werner MX_2A_4 Coordination Complexes', in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Eds.), *Inclusion Compounds*, Academic Press, 1984, pp. 59–103 and references therein.
2. G. M. Sheldrick: SHELXS-86, in G. M. Sheldrick, C. Krueger and R. Goddard (Eds.) *Crystallographic Computing 3*, Oxford University Press, 1985, pp. 175–189.
3. G. M. Sheldrick: SHELX-76, *Program for Crystal Structure Determination*, University of Cambridge, England.
4. C. K. Johnson: ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1965).
5. J. Lipkowski and T. Iwamoto: *J. Incl. Phenom.* **5**, 545 (1987).
6. S. A. Allison and R. M. Barrer: *J. Chem. Soc. A* 1717 (1969).
7. J. Lipkowski, K. Suwińska, G. D. Andreotti and K. Stadnicka: *J. Mol. Struct.* **75**, 101 (1981).